# A Three Parameters Corresponding States Model for Viscosity Prediction of Pure Fluids $^1$

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#### **ABSTRACT**

Predictive and semi-predictive models for viscosity calculation are presently needed and greatly appreciated. In the last few years an Extended Corresponding States (ECS) model was developed formerly for hydrocarbons (HC) and more recently for halocarbon refrigerants (HR). Several attempts were also carried out with a three parameters CS technique leading to models of a prediction accuracy comparable with that of the ECS model. The recent advent of high accuracy viscosity dedicated equations for several HC and for some HR over the entire (r,T) domain of the fluid allows to develop more powerful predictive and semi-predictive models for these classes of fluids, typically nonpolar and polar ones. From these equations it is seen that for non-polar fluids (HC) viscosity conforms to a two parameters CS model. For polar fluids (HR) the deviation is greater, but the general trend is confirmed too. This suggests that there is a potential parallelism among volumetric and transport properties and that the CS techniques formerly developed for volumetric properties can be applied to transport properties too. In the present work a three parameters CS model is then developed importing methods formerly studied for the volumetric representation of fluids. Two fluids of the same family are chosen for both their acentric factor value and for the viscosity dedicated equations availability and, on the basis of the Teja et al. three parameters CS model for volumetric properties, the reduced viscosity of a third fluid of the family is obtained in reduced r,T variables utilising, in a first extent, the Pitzer acentric factor as third parameter. Where the transport property is known at least along the saturation line an improvement is introduced substituting the acentric factor with a temperature dependent correction function fitted on these data. The reached prediction accuracy is comparable with those of the reference fluids equations while both in predictive and semi-predictive mode the amount of input data is anyway very limited. The conversion of the independent variables from (P,T) to (r,T) is obtained through volumetric dedicated EoS utilised, for the fluids of interest, once more in the framework of the Teja et al. three parameters CS. Through the proposed method equivalent dedicated viscosity equations for all the fluids of a family are then obtained from the dedicated equations of only one or two couples of fluids, i.e. two or three fluids, of the same family. Considering the predictive nature of the model and the scattering of the available experimental data, the mean accuracy is good and particularly satisfactory for technical application requirements.

KEY WORDS: acentric factor, alogenated refrigerants, corresponding states, dedicated equations, hydrocarbons, predictive model, pure fluids, three parameters, transport properties, viscosity

#### 1. INTRODUCTION

In the last few years the demand of precise equations for transport properties of fluids is greatly increased and some research groups are producing interesting results. The prediction of viscosity through high accuracy correlations needs as many experimental data sets as possible for the fluids of interest. For those fluids with sufficient data sets distributed on the PrT surface an accurate correlation has furthermore to be obtained in order to substitute direct measurements. This process is inevitably long and heavy.

On the other hand there is the need for a general model for viscosity prediction valid at least for a family of fluids. The only example is at the moment the Extended Corresponding States model for hydrocarbons (TRAPP) [1] and for refrigerants [2], but it is considered by the same Authors much more as an estimation method, with lower accuracy with respect to an individually dedicated equation.

A general model based on a corresponding states technique is here proposed and applied to the alkane and alogenated alkane families of fluids, respectively nonpolar and polar ones.

Moreover any thermophysical property is in general expressed as function of the two independent variables P and T, while it is known that the transport properties are analytically represented as function of r and T. In parallel to the proposed model a conversion has to be provided between the two couples of variables through a thermodynamic model of the higher volumetric accuracy as possible. The high volumetric accuracy of this model is required due to the great sensitivity of the transport properties to density.

For this reason a parallel corresponding states model for thermodynamics will be presented in the following.

#### 2. DEDICATED EQUATIONS FOR PURE FLUIDS VISCOSITY

The correlation of a transport property as function of temperature and density is customarily developed on the residual concept, although there is not a general formulation for the theory on which the transport properties dedicated equations are developed. Following the residual concept in its more general extent viscosity is represented by:

$$h(r,T) = h_0(T) + \Delta_R h(r,T) + \Delta_C h(r,T)$$
(1)

where:

 $h_0(T)$  is a dilute-gas term representing the zero density limit of gas viscosity depending only from the temperature.

 $\Delta_R h(r,T)$  is the residual or excess function. For the majority of the fluids this equation presents only a weak dependence from temperature and, although the elimination of the temperature dependence from the equation cannot be taken as a rule for all substances, this condition is assumed only after an examination of the temperature dependence for each fluid of interest. A compromise between the error introduced with the simplification and the experimental uncertainties has also to be considered. For all the fluids involved in the present study the elimination of the temperature dependence was accepted assuming:  $\Delta_R h = \Delta_R h(r)$ .

 $\Delta_c h(r,T)$  is a critical enhancement function which is effective only in a limited PrT region very close to the critical point. In general this function has for viscosity low significance, also due to the limited availability of experimental data in the region.

Outside the near-critical region eq (1) reduces to the so called background viscosity:

$$\overline{h}(r,T) = h_0(T) + \Delta_R h(r)$$
(2)

The dilute-gas function is developed independently from the residual function. The values of  $h_0(T)$  are not directly experimentally accessible so that they must be obtained through a reduction of viscosity data in the vapor phase at low density. From experimental data reporting the pressure dependence of vapor viscosity, e.g. data along isotherms, the extrapolated values at zero density are calculated and correlated as function of temperature.

The adjustable parameters are obtained fitting an equation of pre-defined analytical form to the generated viscosity data at zero density limit. Several techniques are assumed to develop this form: some are obtained from kinetic theory, fitting only few parameters for the fluid of interest, while other are completely empirical simply best-fitting the generated data.

The residual function  $\Delta_R h(r,T)$  is no more experimentally accessible and its values are obtained as difference between the real value of viscosity and the dilute-gas function and the critical enhancement function, if any, all evaluated at same temperature and density. The generated viscosity values are then correlated by a selected function and several functional forms are proposed here too.

#### 2.1 Hydrocarbons

In the present study the fluids of this family for which a dedicated viscosity equation (1) is needed are methane, n-butane and n-heptane. For these three fluids equations developed on the residual concept, but not yet published, were utilised [3,4].

The data sets assumed for the model fitting, the distribution of both the viscosity data and the residual error of the model, over the PrT surface of the pure, are not presently available.

Because the knowledge of the local prediction accuracy of the dedicated viscosity equations for the reference fluids is fundamental for the characteristics of the final local prediction accuracy of the proposed model an analysis for the three hydrocarbons is afterwards presented.

A validation of the dedicated equation of each hydrocarbon reference fluid, subdividing the PrT surface in liquid, vapor and supercritical region has been done and the results are summarised in Table I. The data utilised are possibly distributed on all the PrT surface of the pure in the limit of the data availability. No statistical error screening was carried out on the data sets and for seek of brevity the numerous sources are not reported in this occasion.

Over the 1067 points considered for the three fluids the AAD is 2.67%.

The results show the error increasing, for all the fluids, toward the critical point, due to the suppression of the critical enhancement function. As general trend the error also increases as much as the pressure becomes higher in the compressed liquid region while in the rarefied vapor region at low temperature an higher error is verified.

As will be seen also in the following these trends are not valid for any data set, but they can be modified following the general measurement accuracy of the particular data set. In fact it has to be pointed out that in general the local prediction accuracy reached by a dedicated viscosity equation is comparable with the uncertainties of the data due to inconsistencies in the data sets.

#### 2.2 Alogenated refrigerants

Among the alogenated refrigerants the two HFC R134a and R152a were chosen as reference fluids for both the availability of viscosity dedicated equations and their acentric factor value, which are enough different to bracket the majority of the fluids of the family, in particular of HFC's.

For the refrigerants family a viscosity equation (2) is utilised for both R134a and R152a. For these fluids the equations validation is not necessary, because a similar information is available from the original papers where the assumed equations are presented.

For R134a [5] an AAD error of 3.38 % over 286 points distributed on the PrT surface was obtained, while for R152a [6] an AAD error of 2.90 % over 646 points also distributed on the PrT surface is reported. In total an overall uncertainty of  $\pm 5$ % for R134a and of  $\pm 3$ % for R152a is assured by the Authors for all the PpT surface considered.

The same comments on the accuracy of the hydrocarbons viscosity equations are valid here too.

## 3. THREE PARAMETERS CORRESPONDING STATES EoS FOR PURE FLUIDS

#### 3.1 Dedicated EoS for pure fluids

In general the modern dedicated EoS are in the great majority of cases of the two analytical forms presented in the following.

The first equation is the 32-term modified Benedict-Webb-Rubin (MBWR32), first proposed by Jacobsen and Stewart, 1972, which has the form:

$$P(r,T) = \sum_{n=1}^{9} a_n(T) r^n + \exp(-C^2) \sum_{n=10}^{15} a_n(T) r^{2n-17}$$
(3)

where  $d = r/r_c$ ,  $r_c$  is the critical density, and the temperature dependence of the coefficients  $a_n(T)$  is:

$$a_{1} = RT \qquad a_{2} = b_{1}T + b_{2}T^{0.5} + b_{3} + \frac{b_{4}}{T} + \frac{b_{5}}{T^{2}} \qquad a_{3} = b_{6}T + b_{7} + \frac{b_{8}}{T} + \frac{b_{9}}{T^{2}}$$

$$a_{4} = b_{10}T + b_{11} + \frac{b_{12}}{T} \qquad a_{5} = b_{13} \qquad a_{6} = \frac{b_{14}}{T} + \frac{b_{15}}{T^{2}} \qquad a_{7} = \frac{b_{16}}{T} \qquad a_{8} = \frac{b_{17}}{T} + \frac{b_{18}}{T^{2}}$$

$$a_{9} = \frac{b_{19}}{T^{2}} \qquad a_{10} = \frac{b_{20}}{T^{2}} + \frac{b_{21}}{T^{3}} \qquad a_{11} = \frac{b_{22}}{T^{2}} + \frac{b_{23}}{T^{4}} \qquad a_{12} = \frac{b_{24}}{T^{2}} + \frac{b_{25}}{T^{3}}$$

$$a_{13} = \frac{b_{26}}{T^{2}} + \frac{b_{27}}{T^{4}} \qquad a_{14} = \frac{b_{28}}{T^{2}} + \frac{b_{29}}{T^{4}} \qquad a_{15} = \frac{b_{30}}{T^{2}} + \frac{b_{31}}{T^{3}} + \frac{b_{32}}{T^{4}}$$

For each pure fluid 32 equation parameters have to regressed from experimental data. This EoS is here utilised for the four alkanes C1, C3, *n*-C4 [7], *n*-C5 [8]. For the equation coefficients reference is made to the original papers.

The second is the Schmidt-Wagner (SW) equation, first proposed by Schmidt and Wagner, 1985 and formulated in the form of the free energy of Helmholtz *a*:

$$a(T, v) = a^{0}(T, v) + a^{r}(T, v)$$
(4)

where  $a^0(T, v)$  is the ideal gas part and  $a^r(T, v)$  the residual function. a(T, v) is then generalised:

$$\Phi(\mathsf{t},\mathsf{c}) = \frac{a}{RT} = \Phi^{o}(\mathsf{t},\mathsf{c}) + \Phi^{r}(\mathsf{t},\mathsf{c})$$
 (5)

with  $d = r/r_c$ ,  $t = T_c/T$ , while for the ideal and real parts it is:

$$\Phi^{0} = \ln(\mathsf{cl}) + a_{1}^{0} + a_{2}^{0} \mathsf{t} + a_{3}^{0} \ln(\mathsf{t}) + \sum_{i=4}^{N_{0}} a_{i}^{0} \mathsf{t}^{a_{i}^{0}}$$
(6)

$$\Phi^{r} = \sum_{i=1}^{N_{0}} a_{i} \mathcal{O}^{d_{i}} \mathsf{t}^{t_{i}} + \sum_{k=1}^{5} \left( \exp(-\mathcal{O}^{k_{k}}) \sum_{i=N_{k-1}+1}^{N_{k}} a_{i} \mathcal{O}^{d_{i}} \mathsf{t}^{t_{i}} \right)$$
(7)

Due to the optimisation method utilised for this equation the particular analytical form of the SW for each fluid is different, because the parameters appearing in both the ideal and real parts, eqs. (6) and (7), are different. This equation is utilised in the proposed model for the two polar fluids R134a and R152a and the forms are taken from [9]. For the equation parameters reference is made to the literature sources. For both fluids successive versions of the same SW equation were refitted later [10,11], but it was controlled that the difference introduced by the updated versions do not affect in any appreciable way the numerical results of this study. Anyway, as will be pointed out afterwards, in the same framework of the proposed model one can change not only the version of the same equation, but also the equation type, as long as a high prediction accuracy is observed.

Table II summarises the fluids of interest, their EoS and the ranges of validity.

#### 3.2 Three parameters CS EoS

Because for heptane, one of the fluids selected for the model here proposed, no dedicated EoS is at the moment available, a suitable thermodynamic model has to be set up for the accurate representation of its thermodynamic behaviour. It is expected that the prediction accuracy of the model for this fluid be of the same level of the dedicated EoS used for the other reference fluids involved in the model.

The three parameters corresponding states model of LK is based on the interpolation of the compressibility factors of two reference fluids, the "simple" and the reference ones, calculated at the same reduced variables of the fluid of interest, as a linear function of the acentric factor of the fluid of interest.

In the case the fluids to represent are components of the same family it is more convenient to substitute the "simple" fluid with a second reference fluid so that both reference fluids belong to the family. The first-order perturbation around a reference fluid, according to the original Pitzer proposal, is maintained in this case too transforming it into a linear interpolation between two reference fluids of the family.

This model, first proposed by Teja [12], is here identified as *modified LK* (MLK) and is formulated as follows:

$$Z(T_r, P_r, \mathcal{N}) = Z^{(r1)}(T_r, P_r) + \frac{\mathcal{N} - \mathcal{N}^{(r1)}}{\mathcal{N}^{(r2)} - \mathcal{N}^{(r1)}} [Z^{(r2)}(T_r, P_r) - Z^{(r1)}(T_r, P_r)]$$
(8)

where  $\sqrt{y^{1}}$   $\sqrt{y^{2}}$  are the acentric factors of the two reference fluids 1 and 2.

The new model requires the previous determination of Z for each of the reference fluids. In this new model both the choice of the reference fluids of the family and then of the EoS adopted for their representation are substantially free. Taking care of a higher volumetric prediction accuracy of the present model this suggests to utilise dedicated EoS for the reference fluids and to choice the reference fluids among those of the family for which dedicated EoS are already available.

Moreover from classical thermodynamics it is shown that the linear dependence of Z on the acentric factor  $\omega$ , reported by the MLK model, is repeated for the adimensional residual function  $\Delta m^R$  of any molar thermodynamic property m:

$$\Delta m^{R} = \left(\Delta m^{R}\right)^{(r1)} + \frac{\bigvee \bigvee \bigvee^{r}}{\bigvee \downarrow^{r}} \left[ \left(\Delta m^{R}\right)^{(r2)} - \left(\Delta m^{R}\right)^{(r1)} \right]$$

$$\tag{9}$$

The vapor pressure of a pure fluid can be represented through the classical relation:

$$\int_{t}^{s} (T, P) = \int_{v}^{s} (T, P) \tag{10}$$

Applying eq. (9) to the Gibbs function g each one of the functions  $\Delta g^R$  to be introduced in eq. (10) can be obtained as a linear interpolation in  $\omega$  of the adimensional Gibbs residual functions of the two reference fluids.

An analysis of the volumetric prediction accuracy of the model has shown that in general the model is less precise in the dense phase with the error deviation increasing from the condition of saturated liquid toward the higher pressures [13,14,15]. It was also verified that on the compressed liquid surface among the two variables T and P is the increase of the first one to raise to a greater extent the error. A correction of the liquid density prediction as a function of temperature has hence been successfully introduced in the former model [14,15].

A new model is then proposed:

$$Z(T_r, P_r) = Z^{(r1)}(T_r, P_r) + \frac{\checkmark \checkmark (T_r) - \checkmark \checkmark^{(r1)}}{\checkmark (T_r) - \checkmark \checkmark^{(r1)}} \left[ Z^{(r2)}(T_r, P_r) - Z^{(r1)}(T_r, P_r) \right]$$
(11)

From density data of the fluid of interest at saturated liquid conditions an accurate correlation is obtained through regression:

$$\Gamma_{l}^{s} = \Gamma_{l}^{s}(T) \tag{12}$$

At each temperature, in the range of validity of eq. (12), the saturated liquid density is calculated and introduced into the left side of eq. (11), where, with a tentative value of pressure, an approximate value of  $\bigvee_{r}^{*}$  is obtained which yields a new pressure value through the equilibrium condition (10). Proceeding up to pressure convergence a value of  $\bigvee_{r}^{*}$  is iteratively obtained at each T. The function  $\mathcal{G}(T_r)$  is afterwards defined:

$$Q(T) = \frac{\bigvee_{r}^{*}(T_{r})}{\bigvee_{r}} \tag{13}$$

with an analytical form individually determined for each fluid of interest through an accurate regression of generated values of g. Introducing the eq. (13) into eq. (11) makes the model to reproduce the saturated liquid density with only the residual errors of the two regressions, eqs. (12) and (13).

Only from a set of saturated liquid density data for the fluid of interest, besides the classical critical parameters, an accurate thermodynamic model is then obtained. It is also evident that the original three parameters corresponding states model has been reconverted into a two parameters one, as eq. (11) shows.

#### 3.2.1 Thermodynamic representation of *n*-C7

Because for alkanes the fluids with available dedicated EoS are all those from C1 to n-C5 a rational choice of the two reference fluids for the thermodynamic representation of heptane is necessary. Heptane has an acentric factor of 0.349 while the six alkanes from C1 to n-C5 have  $\omega$  increasing in value with the number of carbon atoms in the molecule, ranging from 0.01086 of C1 to 0.251 of n-C5. The best choice is to extrapolate toward n-C7 from n-C5, selecting the fluid at left of n-C5 having a difference in  $\omega$  from n-C5 similar to that between n-C5 and n-C7. The choice is C3 which has  $\omega$ =0.153.

A model is then developed for heptane following the proposed theory. Two sets of liquid density data with a total of only 11 points were assumed [16,17] and the  $\mathcal{G}(T)$  function was obtained and introduced into the model.

#### 3.2.2 Validation of the CS model for *n*-C7

Because the prediction accuracy of the thermodynamic model for *n*-heptane has to be of a similar order of those of the dedicated EoS of the other reference fluids, a validation of the model has been obtained over several data sets and is here presented by the summarised results presented in Table III. No data set in the vapor phase was found.

The very high degree of volumetric accuracy reached with the semi-predictive model shows both the effectiveness of the new thermodynamic model and its suitability to be utilised here, because its accuracy is comparable with those of the dedicated EoS of the other reference fluids.

## 4. CONFORMALITY OF COMPRESSIBILITY FACTOR AND REDUCED VISCOSITY

Representing the compressibility factors obtained from dedicated EoS for fluids of a same family in a two parameters corresponding states format usually they tend to conform, as Figs. 1 and 3 show for some hydrocarbons and alogenated refrigerants respectively. This demonstrates that for these two families an evident volumetric conformality exists among the components. The residual deviation has to be corrected introducing a further parameter,  $\omega$  of Pitzer [18,19,20,12] or, alternatively, a "tuning function"  $\bigvee_{r}^{*}(T_{r})$  [14,15].

If a similar conformality exists for the reduced viscosity the techniques developed for three parameters corresponding states thermodynamics can be transferred to viscosity. The Figs. 2 and 4 demonstrate such behaviour for the two families allowing to proceed for viscosity as for density. Some former tentatives are also present in literature [21,22].

#### 5. THREE PARAMETERS CORRESPONDING STATES FOR VISCOSITY

As shown in the former paragraphs, the compressibility factor Z presents, for the fluids of a same family, a good "conformality" already in the domain of the two parameters corresponding states principle and the residual inaccuracy is dramatically reduced through the introduction of a third parameter, the acentric factor VV or moreover the function Q(T) regressed from saturated liquid density values for the each pure [14,15].

Because the reduced viscosity  $h_r$ , similarly to Z, tends to conform enough well to the two parameters corresponding states principle for a same family of fluids, it is supposed that the same refinements of the thermodynamic model for Z, exposed formerly, would be suitable to develop for viscosity a model similar in the framework to that already utilised with success for Z.

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In a first stage the proposed model is then:
$$\left[ h_r(P_r, T_r, \mathbf{w}) = h_r^{(r_1)} \left[ r^{(r_1)}, T^{(r_1)} \right] + \frac{\mathbf{w} \cdot \mathbf{w}^{(r_1)}}{\mathbf{w}^{(r_2)} - \mathbf{w}^{(r_1)}} \left\{ h_r^{(r_2)} \left[ r^{(r_2)}, T^{(r_2)} \right] - h_r^{(r_1)} \left[ r^{(r_1)}, T^{(r_1)} \right] \right\} \right] \\
r^{(r_1)} = r^{(r_1)} \left( P_r, T_r \right) \\
r^{(r_2)} = r^{(r_2)} \left( P_r, T_r \right) \\
T^{(r_1)} = T_r T_c^{(r_1)} \\
T^{(r_2)} = T_r T_c^{(r_2)}$$
(14)

where  $\vee \vee$  is the Pitzer acentric factor, same as in the Z model, and  $h_r^{(r1)}[r^{(r1)},T^{(r1)}]$  and  $h_r^{(r2)}[r^{(r2)},T^{(r2)}]$  are the dedicated equations of viscosity in reduced form for the two reference fluids r1 and r2 of the same family, valid for the whole PrT surface of these fluids. The viscosity coming from the dedicated equations is reduced with the same pseudo-critical viscosity  $H_c$  utilised to express the residual function  $\Delta_R h(r,T)$  in dimensionless form in eqs. (1) and (2):

$$H_c = \frac{M^{1/3} P_c^{2/3}}{R^{1/6} N_A^{1/3} T_c^{1/6}} \tag{15}$$

where  $T_c$  and  $P_c$  are the absolute temperature and pressure, M the molar mass and  $N_A$ the Avogadro number.

In this formulation the model is predictive, because only the critical parameters and the acentric factor are to be given as input for a generic fluid. Furthermore in the model, represented by the system (14), the only independent variables are  $T_r$  and  $P_r$  of the fluid of interest.

Any thermophysical property is in general expressed as function of the two independent variables P and T, while it was shown that the transport properties are analytically represented as function of r and T. In parallel to the proposed model a conversion has to be provided between the two couples of variables through a thermodynamic model of the higher volumetric accuracy as possible. The high volumetric accuracy of this model is required due to the great sensitivity of the transport properties to density.

For the proposed transport properties model only the thermodynamic models for the two reference fluids r1 and r2 are required while these two models can also be of different analytical form.

Looking at the model prediction accuracy a certain decrease is noted in the liquid phase and in particular for refrigerants, but a precise general trend is not ascertained for both families of fluids. The relative inconsistency of the experimental data sets may be more important than the model accuracy so that this looks to be insensitive to the P and T variables. A significant increase of the mean accuracy was noted after improving the model as in the following.

In a second stage the Pitzer acentric factor  $\vee \vee$  is then replaced in the model with  $\vee_{\Gamma}^*(T_r)$  through a "tuning function"  $J(T_r)$ , regressed from saturated liquid viscosity values for the each pure, making the new model similar to the former modified one for Z.

From viscosity data at saturated liquid condition of the fluid of interest an accurate correlation as an individual continuous function of temperature is obtained through regression:

$$\mathsf{h}_{t}^{s} = \mathsf{h}_{t}^{s}(T) \tag{16}$$

At each temperature, in the range of validity of eq. (16),  $h_l^s$  is known while from the three parameters thermodynamic model, eqs. (11) to (13), the vapor pressure is calculated. From the system (14) a value of  $\bigvee_{l}^{*}$ , replacing now  $\bigvee_{l}$  is obtained.

A function  $J(T_r)$  is then defined:

$$J(T_r) = \frac{\sqrt{r}(T_r)}{\sqrt{r}} \tag{17}$$

with similar characteristics of the former function  $\mathcal{G}(T_r)$ , eq. (13). Introducing eq. (17) into the first equation of system (14) this is transformed into:

$$h_{r}(P_{r}, T_{r}) = h_{r}^{(r1)} \left[ r^{(r1)}, T^{(r1)} \right] + \frac{\sqrt{r}(T_{r}) - \sqrt{r}}{\sqrt{r}^{(r2)} - \sqrt{r}} \left\{ h_{r}^{(r2)} \left[ r^{(r2)}, T^{(r2)} \right] - h_{r}^{(r1)} \left[ r^{(r1)}, T^{(r1)} \right] \right\}$$

$$(18)$$

The model reproduces the saturated liquid viscosity with only the residual errors of the two regressions, eqs. (16) and (17) and is suitable to represent viscosity on any point of the PrT surface of a fluid of the family in the same ranges of the dedicated equations of the reference fluids. In such a way from a set of saturated liquid viscosity data for the fluid of interest, besides the classical critical parameters and the Pitzer acentric factor, an accurate viscosity model is obtained.

Also in this case one can see that the original three parameters corresponding states model has been reconverted into a two parameters one, as shown by eq. (18).

### 5.1 Validation of the viscosity model with $\bigvee_{r}^{*}(T_r)$

The prediction accuracy of the proposed viscosity models is now to be discussed. This validation study is restricted by the experimental data availability. For each family a selection of fluids is done in advance. While for hydrocarbons the choice is practically obliged by the increment of the carbon atoms in the alkanes molecule, for refrigerants a choice is operated for four fluids: the two HCFC R22 and R123 and the two HFC R32 and R125. No relation with the international legislation about the limitations of refrigerants utilisation is here considered.

The advantage of the introduction of  $\bigvee_{r}^{*}(T_r)$  is here discussed only for two fluids, the hydrocarbon n-C5 and the refrigerant R32, and the results are shown in the following Tables IV and V. For both only data out of saturation and with  $T < T_c$  and  $P < P_c$  are assumed making clear the action of  $\bigvee_{r}^{*}$ . It is evident the general increase of accuracy from the new AAD and bias values, in particular for the liquid phase and even more for the polar refrigerant R32. The final results are similar for both fluids and are comparable with the experimental inaccuracy of the better data sets.

#### 5.1.1 Validation for alkanes

Seven alkanes were considered with increasing number of carbon atoms. The results of the model validation are presented in Table VI for a total of 2373 points on all the PrT surface. For *n*-C8 the results, obtained through extrapolation, are similar to those of the lighter alkanes obtained through interpolation. Only for *n*-C10 a certain accuracy decrease seems to begin. Going forward another reference fluid would then be needed.

Because for n-C12 liquid viscosity data at saturation were not available and for it the results were obtained with  $\searrow 6$  Pitzer, the model with  $\searrow 7$  ( $T_r$ ) was tested for alkanes on 2308 points producing a total AAD of 3.72%.

#### 5.1.2 Validation for alogenated refrigerants

Four alogenated alkanes were studied and the results are presented in Table VII for a total of 1063 points in all the phases.

Over the whole data base the present model with  $\bigvee_{r}^{*}(T_r)$  yields a total AAD of 3.97%. Except two data sets with evident lower experimental accuracy the results level is similar to that of hydrocarbons. Here R22 is obtained through extrapolation, but no evident accuracy decrease is seen with respect to the other refrigerants for the liquid phase, while for all three vapor sources a similar but worse value is noted. Here too the data experimental uncertainties are probably more determinant on the final result.

The values of maximum error found for refrigerants indicate that here too more reliable validations would be obtained after a data screening.

For alkanes the AAD passes from 2.67% for the three reference dedicated equations to 3.72% for the six fluids considered in Table VI. For refrigerants the AAD changes from 3.38% for R134a and 2.90% for R152a dedicated equations to 3.97% for the four fluids considered. With respect to the examined points the proposed model looses

roughly a point of AAD with respect to the reference equations assumed. A data screening would probably reduce these figures lowering the differences.

Considering the total of 3371 points formed by 2308 points for alkanes and by 1063 points for refrigerants an overall AAD value of 3.80% is obtained.

#### 5.2 Comparison with dedicated equations for viscosity

For those fluids for which a dedicated viscosity equation is available, but different from those involved as reference fluids in the present model, a comparison is possible between the prediction accuracy of the proposed model and the dedicated equation.

For hydrocarbons a viscosity equation recently published for propane [23] is here considered, while for refrigerants an equation for R123 [24] is assumed.

For each of the fluids a comparison is presented between the model and the dedicated equation. In Tables VIII and IX the deviations of the present model with respect to the same set of experimental data assumed for the validation of the proposed model are reported.

The comparison of these results with those of Tables VI and VII for the same fluids indicates that the proposed model reaches an AAD roughly 25% higher with respect to the two dedicated equations: this has to be regarded as a good result considering the semi-predictive nature of the model with respect to the massively correlative dedicated equations. Few viscosity data at saturation are enough to yield the results reported for the present model. Moreover, due to the high maximum errors in general found a screening of the data limiting their scattering would be necessary to obtain more reliable validations and comparisons.

#### 6. CONCLUSIONS

The calculation of pure-component viscosity of families of polar and nonpolar fluids is obtained through a new model extending an improved corresponding states technique for thermodynamics to viscosity prediction. The model requires as input the critical parameters T<sub>c</sub>, P<sub>c</sub> and few experimental data of saturated liquid density and viscosity in the temperature range of interest. Otherwise, but at a lower level, the input experimental data can be replaced by the Pitzer acentric factor. The model, of *semi-predictive* or *predictive* nature, following the two cases, is then applied to the alkane and alogenated alkane families of fluids, respectively nonpolar and polar ones.

Agreement between predicted and experimental viscosity is quite good and with an accuracy level, for both families, comparable with the single fluid dedicated viscosity equations presently available.

Because the model basically rely on the accuracy of the dedicated equations of the reference fluids, with a more limited effect from the tuning on saturated liquid viscosity data of the fluid of interest, it can be improved only refining those dedicated equations. Through this model equivalent dedicated equations would then be available for the components of each family limiting the experimental and correlative work on only two or three fluids per family.

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Table I. Global results for validation of viscosity dedicated equations for the reference fluids methane, n-butane and n-heptane<sup>a</sup>.

Fluid	Phase	AAD	Bias	Max	NPT
	1	4.0	-1.7	36.6	94
C1	V	3.8	-0.7	14.5	25
	sc	3.0	-1.6	33.0	77
	overall	3.6	-1.5	33.0	196
	1	1.3	0.43	13.9	28.6
n-C4	V	3.1	1.6	17.0	131
	sc	2.8	0.7	11.8	51
	overall	2.0	0.8	17.0	468
	1	2.4	-0.1	11.4	313
<i>n</i> -C7	V	4.8	-1.6	30.3	77
	sc	6.2	-1.4	33.2	13
	overall	3.0	-0.4	33.2	403

<sup>&</sup>lt;sup>a</sup> Phase: l=liquid, v=vapor, sc=supercritical. Error: AAD=Average Absolute Deviation (%), Bias=bias (%), Max=maximum error (%); NPT=number of experimental points.

Table II: Fluids of interest, for each of the two families, with assumed dedicated EoS.

Fluid	Reference	Temperature	Pressure range	Type of dedicated		
		range [K]	[MPa]	EoS		
	Hydrocarbons					
C1	[7]	up to 600	up to 200	32-term MBWR		
C3	[7]	up to 600	up to 100	32-term MBWR		
n-C4	[7]	up to 500	up to 70	32-term MBWR		
n-C5	[8]			32-term MBWR		
		Alogenated rej	frigerants			
R134a	[9]	170-453	up to 70	Schmidt-Wagner		
R152a	[9]	160-433	up to 30	Schmidt-Wagner		

Table III. Validation of accuracy of the thermodynamic model for n-heptane over density values<sup>a</sup>.

Fluid	Phase	Range P [MPa]	Range T [K]	AAD	Bias	Max	NPT
	1	0.1-70	188-573	0.5	-0.3	2.2	444
<i>n</i> -C7	sc	2.6-32	548-623	0.8	-0.5	2.7	35
	overall	0.1-70	188-623	0.5	-0.3	2.7	479

<sup>&</sup>lt;sup>a</sup> Phase: l=liquid; sc=supercritical; Error: AAD=Average Absolute Deviation (%), Bias=bias (%), Max=maximum error (%); NPT=number of experimental points.

Table IV. Effect of the introduction of the  $\bigvee_{r}^{*}(T_r)$  into the viscosity model for n-C5<sup>a</sup>. Data: out of saturation, T<T<sub>c</sub>, P<P<sub>c</sub>.

Phase	AAD	Bias	Max	NPT				
	Model with ω Pitzer							
1	2.3	0.3	20.2	104				
v	2.43	1.6	-5.6	68				
	Model with $\bigvee_{r}^{*}(T_{r})$							
1	1.7	0.1	20.2	104				
V	2.35	1.7	5.2	68				

Table V. Effect of the introduction of the  $\bigvee_{r}^{*}(T_r)$  into the viscosity model for R32<sup>a</sup>. Data: out of saturation, T<T<sub>c</sub>, P<P<sub>c</sub>.

	,							
Phase	AAD	Bias	Max	NPT				
	Model with ω Pitzer							
1	9.3	8.5	19.8	36				
v	3.3	-3.2	14.5	59				
	Model with $\bigvee_{r}^{*}(T_{r})$							
1	1.7	-0.02	7.5	36				

-2.0

2.1

4.7

59

<sup>&</sup>lt;sup>a</sup> Phase: l=liquid, v=vapor; Error: AAD=Average Absolute Deviation (%), Bias=bias (%), Max=maximum error (%); NPT=number of experimental points.

Table VI. Global results for viscosity prediction of alkanes with the present model<sup>a</sup>.

Fluid	Phase	Range P [MPa]	Range T [K]	AAD	Bias	Max	NPT
	1	0.2-69	150-303	3.5	1.3	19.5	147
C2	V	0.1-4.9	288-423	4.1	3.7	15.3	200
	sc	4.9-69	305-423	5.1	-1.5	17.4	296
	overall	0.1-69	150-423	4.4	0.8	19.5	643
	1	0.3-55	183-370	3.3	-1.5	19.8	161
C3	V	0.1-4.1	277-477	5.5	4.4	17.1	54
	sc	5-55	377-477	4.0	0.7	10.5	59
	overall	0.1-55	150-477	3.9	0.1	19.8	274
	1	0.1-226	173-465	2.2	-0.4	20.2	412
<i>n</i> -C5	V	0.1-3.2	310-510	2.4	2.0	6.5	107
	sc	3.4-55	470-510	3.2	-3.7	6.5	85
	overall	0.1-226	150-510	2.4	-0.4	20.2	604
	1	0.1-201	174-463	3.3	-0.1	13.6	266
n-C6	V	0.1-0.7	348-424	1.4	1.4	2.3	17
	sc	-	-	-	-	-	-
	overall	0.1-201	174-463	3.1	0.0	13.6	283
	1	0.1-175	211-558	4.1	-1.7	17.9	291
<i>n</i> -C8	V	0.1	403-569	3.5	1.9	7.0	39
	sc	2.9-49	569	7.4	3.0	13.7	10
	overall	0.1-175	211-569	4.1	-1.3	17.9	340
	1	0.1-152	240-510	6.3	-1.8	26.6	151
<i>n</i> -C10	V	0.007-0.1	277-477	1.8	-0.9	5.0	13
	sc	-	-	-	-	-	-
	overall	0.007-152	240-510	5.9	-1.7	26.6	164
	1	0.1-121	262-425	16.3	-3.9	88.2	65
<i>n</i> -C12*	V	-	-	-	ı	-	ı
	sc	-	-	-	ı	-	-
	overall	0.1-121	262-425	16.3	-3.9	88.2	65

<sup>\*</sup> no data available of saturated liquid viscosity, results obtained with ∨∕of Pitzer.

Table VII. Global results for viscosity prediction of alogenated refrigerants with the

present model<sup>a</sup>.

Fluid	Phase	Range P [MPa]	Range T [K]	AAD	Bias	Max	NPT
	1	1.3-21	240-333	3.0	2.0	17.9	94
R22	V	0.1-5	243-413	6.2	2.8	19.6	269
	sc	5.5-8	383-413	10.3	-10.3	18.1	12
	overall	0.1-21	240-413	5.5	2.2	19.6	375
	1	1-13	300-400	3.0	-2.2	8.7	41
R123	V	0.1-3.5	300-513	3.4	2.6	8.2	273
	sc	4-7	473-513	10.3	-10.3	23.6	19
	overall	0.1-13	300-513	3.7	1.3	23.6	333
	1	0.2-15	231-348	1.3	-0.2	7.5	88
R32	V	0.1-5.7	223-423	3.1	-1.5	8.5	143
	sc	6-10	373-423	3.0	-2.2	5.8	27
	overall	0.1-15	223-423	2.5	-1.1	8.5	258
	1	2.5-15	216-333	3.2	-0.2	16.1	81
R125	V	0.09	220-366	1.6	0.3	4.3	16
	sc	-	-	-	-	-	-
	overall	0.09-15	216-366	2.9	-0.1	16.1	97

<sup>&</sup>lt;sup>a</sup> Phase: l=liquid, v=vapor, sc=supercritical. Error: AAD=Average Absolute Deviation (%), Bias=bias (%), Max=maximum error (%); NPT=number of experimental points.

Table VIII. Prediction accuracy of the viscosity dedicated equation for *propane* over the same sets of data assumed for the validation of our model<sup>a</sup>.

Fluid	Phase	Range P [MPa]	Range T [K]	AAD	Bias	Max	NPT
	1	0.3-55	183-370	2.5	-0.3	10.0	161
C3	V	0.1-4.1	277-477	2.5	0.2	15.7	54
	sc	5-55	377-477	4.3	4.3	17.8	59
	overall	0.1-55	183-477	2.9	0.8	17.8	274

Table IX. Prediction accuracy of the viscosity dedicated equation for *R123* over the same sets of data assumed for the validation of our model<sup>a</sup>.

Fluid	Phase	Range P [MPa]	Range T [K]	AAD	Bias	Max	NPT
	1	1-13	300-400	1.6	-1.0	4.4	41
R123	V	0.1-3.5	300-513	2.8	-2.8	7.5	273
	sc	4-7	473-513	5.6	-5.6	17.2	19
	overall	0.1-13	300-513	2.8	-2.7	17.2	333

<sup>&</sup>lt;sup>a</sup> Phase: l=liquid, v=vapor, sc=supercritical; Error: AAD=Average Absolute Deviation (%), Bias=bias (%), Max=maximum error (%); NPT=number of experimental points.

- Fig. 1. Compressibility factor of methane, propane and *n*-butane in two parameters corresponding states format.
- Fig. 2. Reduced viscosity of methane, propane and n-butane in two parameters corresponding states format.
- Fig. 3. Compressibility factor of R134a and R152a in two parameters corresponding states format.
- Fig. 4. Reduced viscosity of R134a and R152a in two parameters corresponding states format.







